

Edward T. Urbansky

U.S. Environmental Protection

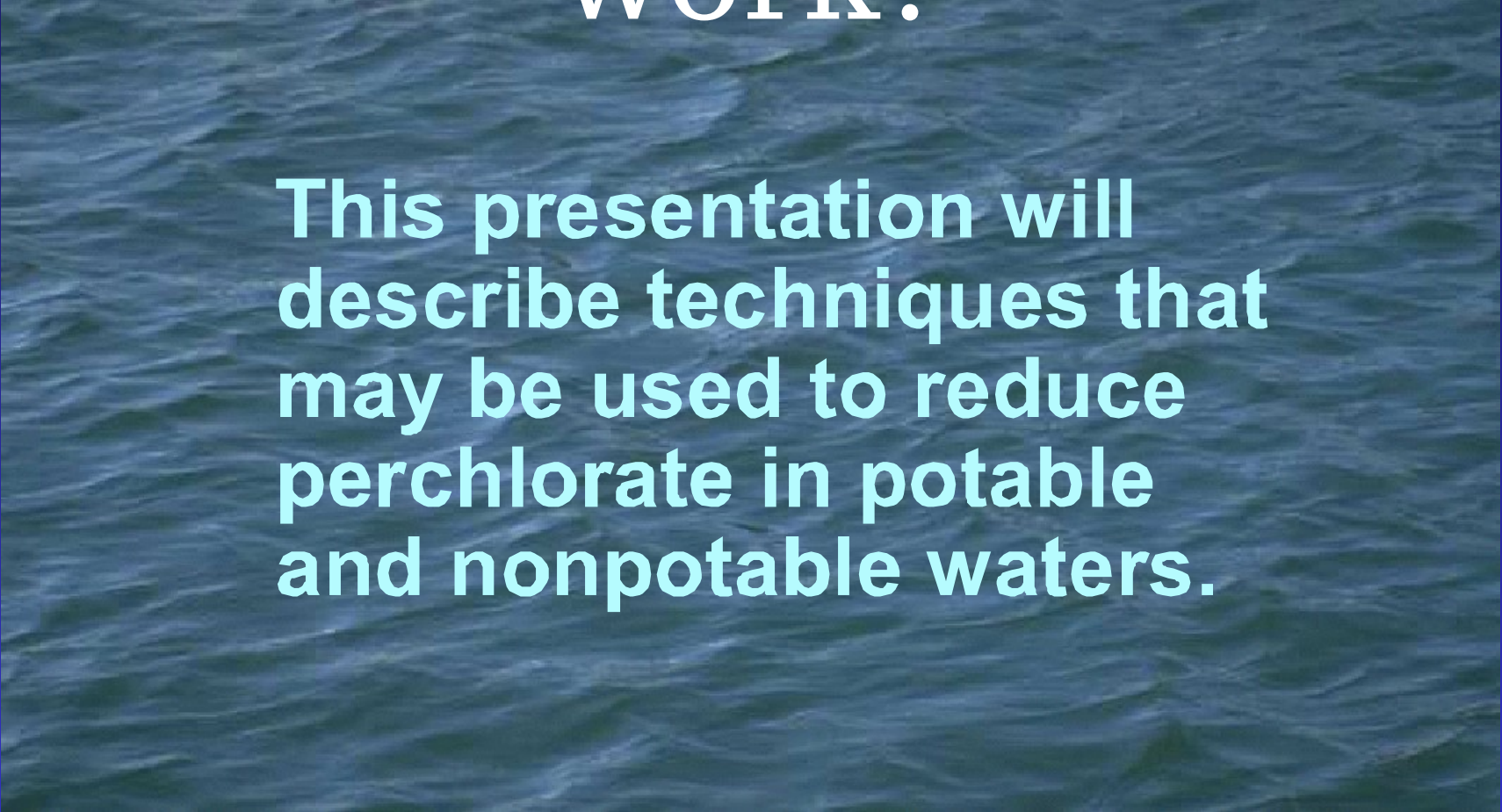
National Risk Management Research Laboratory
Water Supply and Water Resources Division



Cincinnati, Ohio 45268



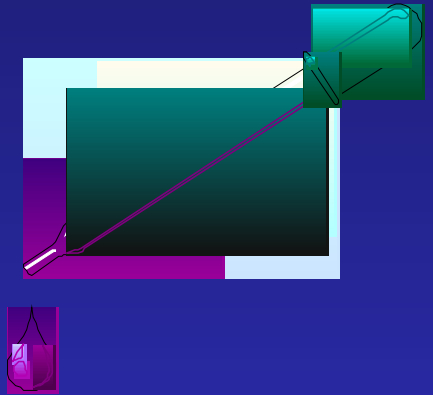
What techniques will work?



**This presentation will
describe techniques that
may be used to reduce
perchlorate in potable
and nonpotable waters.**

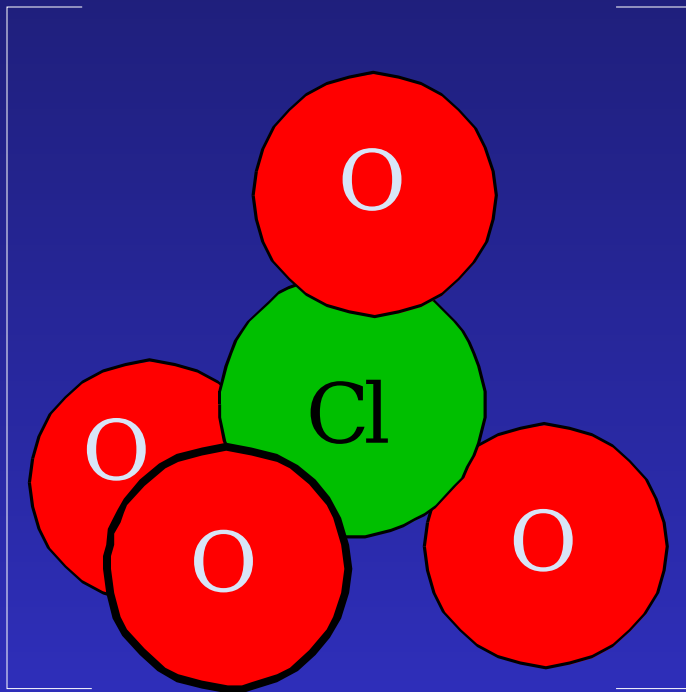
Approach

There is no one technique that will work for every case.



There is no standard or benchmark for evaluating performance.

About Perchlorate



1-

P An oxyanion of chlorine

P A strong oxidizing agent
(thermodynamics)

P A very sluggish species
(kinetics)

Chlorine Species

Name	Oxidation State	Formula
Perchlorate	+7	ClO_4^-
Chlorate	+5	ClO_3^-
Chlorite	+3	ClO_2^-
Hypochlorite	+1	ClO^-
Dichlorine	0	Cl_2
Chloride	-1	Cl^-

↑
*Increasing
oxidizing strength*

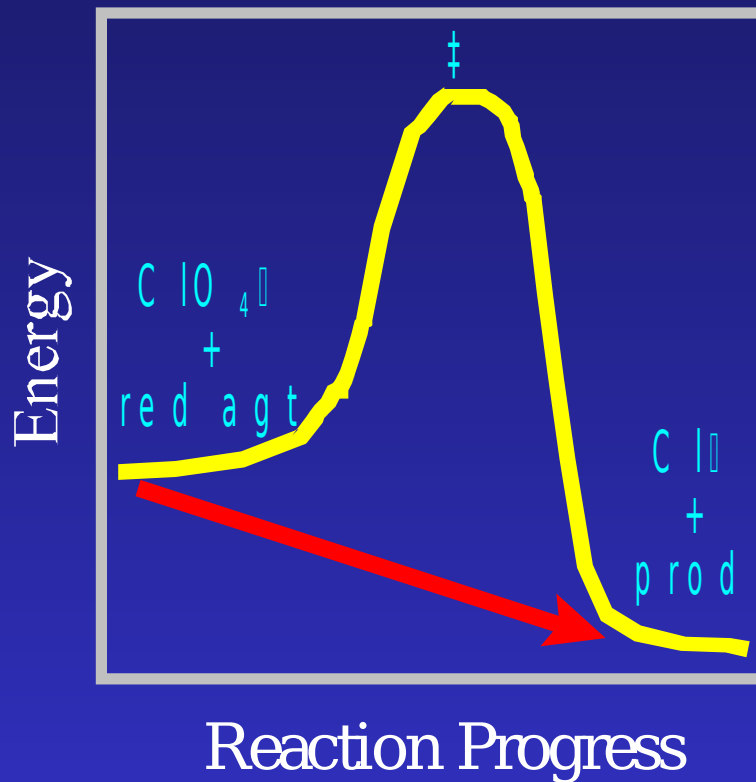
Chemical Reduction



$$E^\circ = 1.287 \text{ volts}$$

A reducing agent transfers electrons to the chlorine atom in a perchlorate ion, converting it to chloride.

Perchlorate Lability



In general, perchlorate reduction is very slow even though perchlorate is a strong oxidizing agent.

Common reductants (e.g., thiosulfate, sulfite) show no measurable reaction.

Labile Reducing Agents

A number of air-sensitive metal species can reduce perchlorate, but they cannot be used directly in water treatment because they are still too slow and their products would have to be removed.

**Titanium(III)
CH₃ReO₂**

Methylrhenium dioxide,

**Vanadium(II, III) Dimolybdenum(III),
Mo₂6+**

Chromium(II)

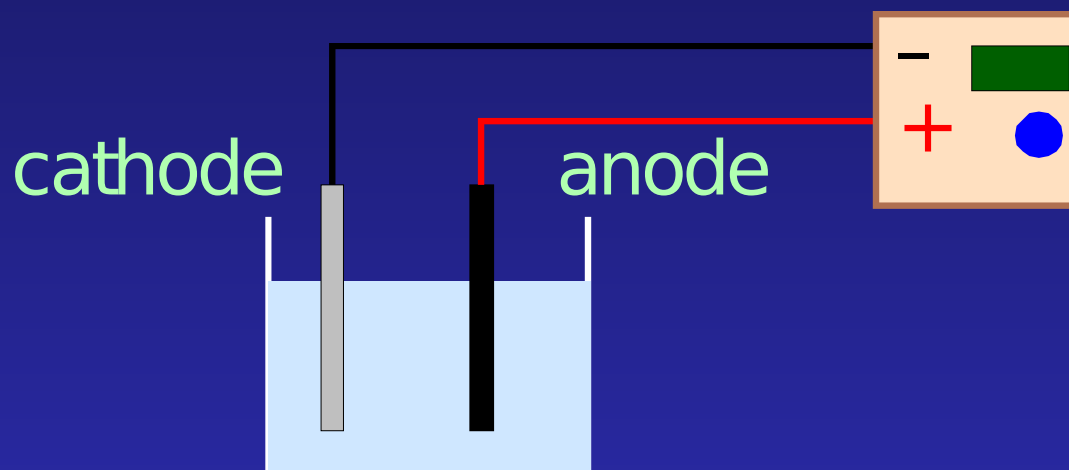
Molybdenum(III)

Chemical Reduction: Problems

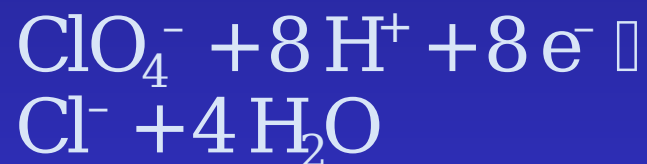
- Expense of materials
- Slowness of reaction
- Toxicity of by-products
- Removal of by-products



Electrochemical Reduction



Reduction

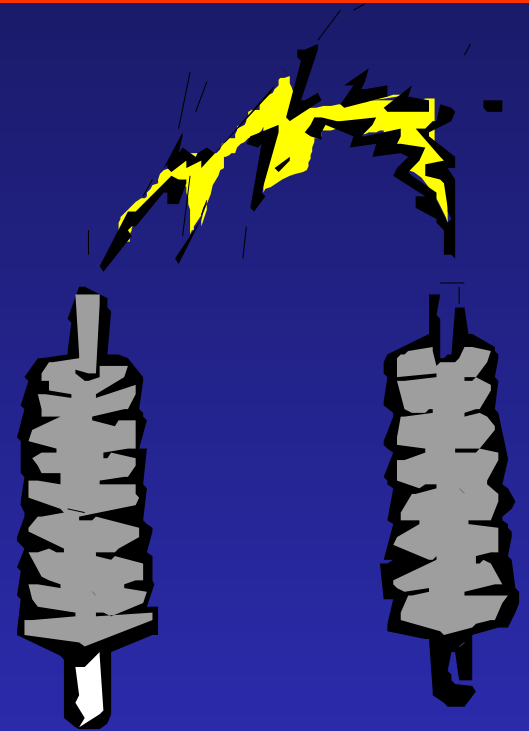


Oxidation



Electrochemistry: Anodes

- Tungsten carbide
- Ruthenium
- Platinum
- Aluminum
- Titanium
- Aluminum oxide
- Carbon (doped with Al_2O_3 or Cr_2O_3)



Electrochemical Reduction

- **Advantages**

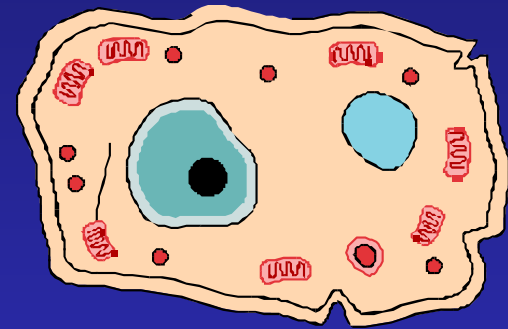
- Nontoxic by-products
- Well-known technique

- **Disadvantages**

- Construction/implementation expense
- Operation expense (electricity)
- Electrolysis of water
- Slowness (reaction and diffusion)
- Safety (high voltage)

Biological Reduction

The use of biological organisms, especially bacteria, to chemically reduce perchlorate to other chemical species



Perchlorate-reducing
bacteria

Ideonella dechloratans

Proteobacteria

Vibrio dechloraticans Cuzenove B-1168

Wolinella succinogenes HAP-1

Biological Reduction

USAF, Tyndall AFB, Florida

The bacterium *Wolinella succinogenes* is capable of using perchlorate as an oxidizing agent (electron acceptor) for metabolism.

The USAF and AF Research Labs have developed a bioreactor for this purpose.



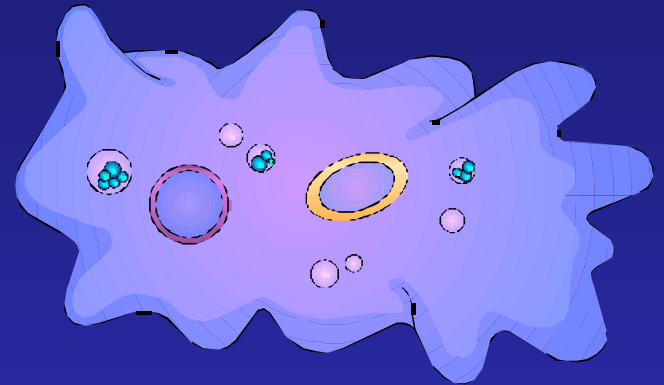
Biological Reduction

- **Advantages**

- Nontoxic by-products
- Versatility
- Speed

- **Disadvantages**

- Acceptance
- Regulatory barriers
- Construction/implementation costs
- Hardiness of bacteria



Biochemical Reduction

- Bacteria use a biological catalyst or enzyme, called a reductase, to reduce perchlorate.
- It may be possible to purify this enzyme and use it directly as a reactant for chemical reduction (addition or tethering).
- Perchlorate reductases evolved from nitrate reductases used by nitrogen-fixing bacteria (e.g., those in legumes).

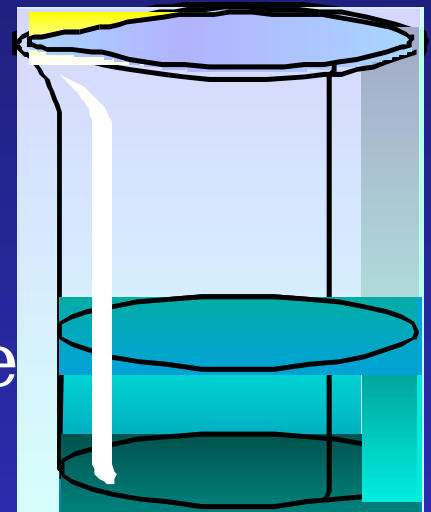
Biochemical Reduction

- **Advantages**

- No toxic perchlorate by-products
- Fast reaction time
- High effectiveness

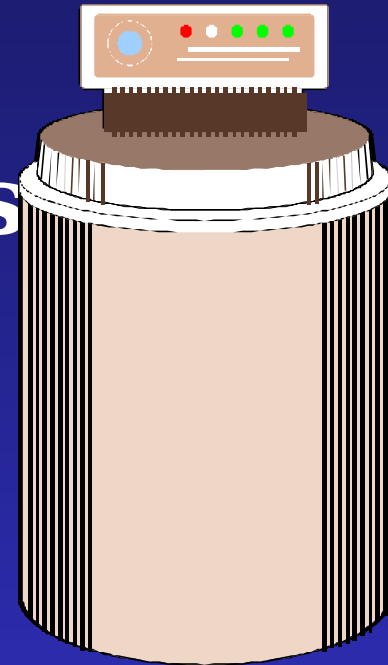
- **Disadvantages**

- High expense in producing e
- High maintenance
- Difficult implementation
- Enzyme by-products unstudied



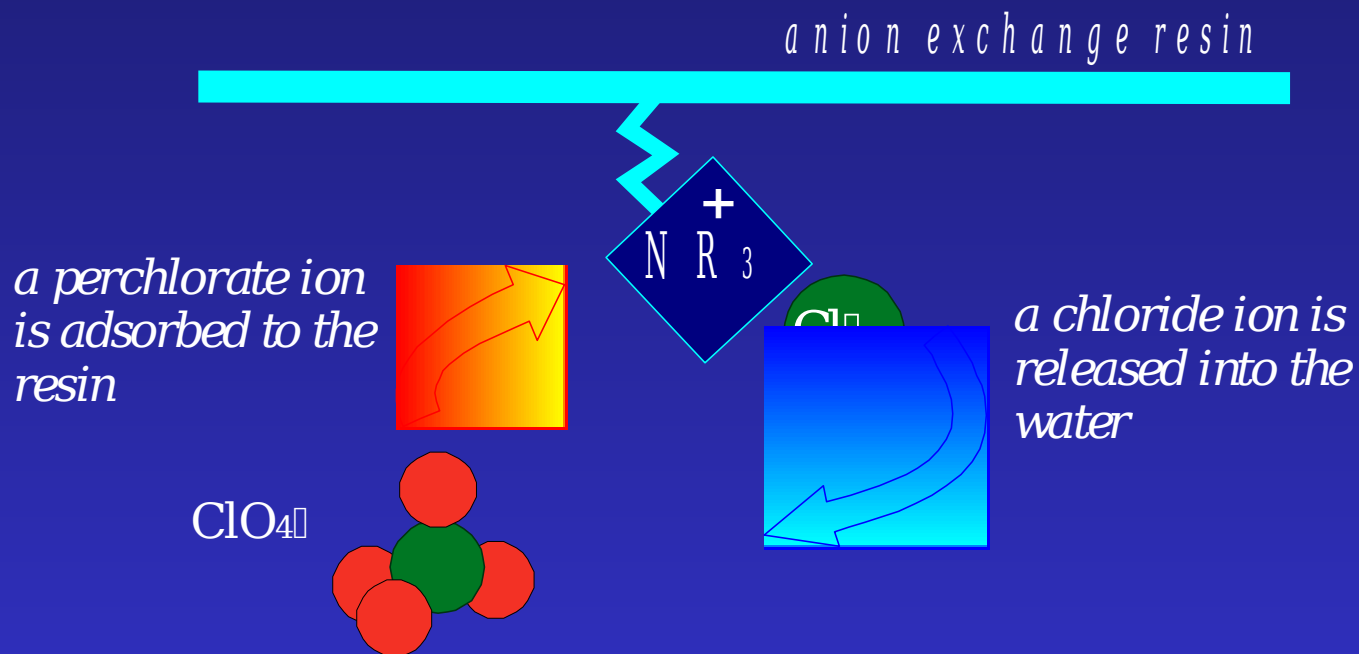
Physical Separation

- **Anion exchange**
- **Membrane processes**
 - Nanofiltration
 - Reverse osmosis
 - Electrodialysis



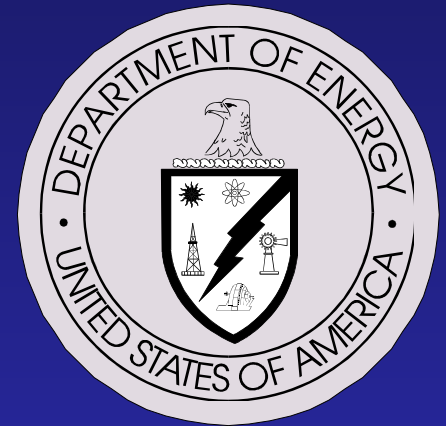
Anion Exchange

A positively charged resin is used to exchange the perchlorate ion for a harmless chloride ion.



Ion Exchange for Pertechnetate

Oak Ridge National Laboratory
Oak Ridge, Tennessee



Selective pertechnetate (TcO_4^-)
removal to parts per trillion
(pg mL^{-1}) levels

Ion Exchange for Nitrate

Anion exchange is used to remove nitrate from water.

- Nitrate-selective resins already exist. NO_3^-
- Perchlorate and nitrate have similar physical properties (charge, size, aquation).
- Therefore, these resins are expected to be effective in removing perchlorate.
- However, permissible nitrate concentrations are much higher than the perchlorate action level.

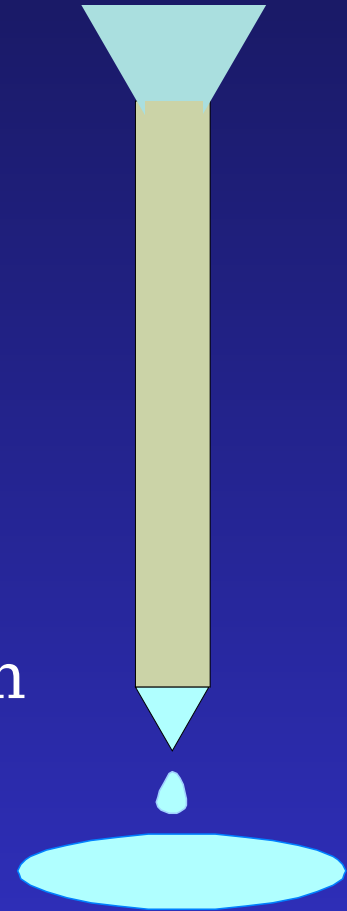
Anion Exchange

- **Advantages**

- Reasonable operating costs
- Well-developed technique
- Easy implementation
- Effectiveness

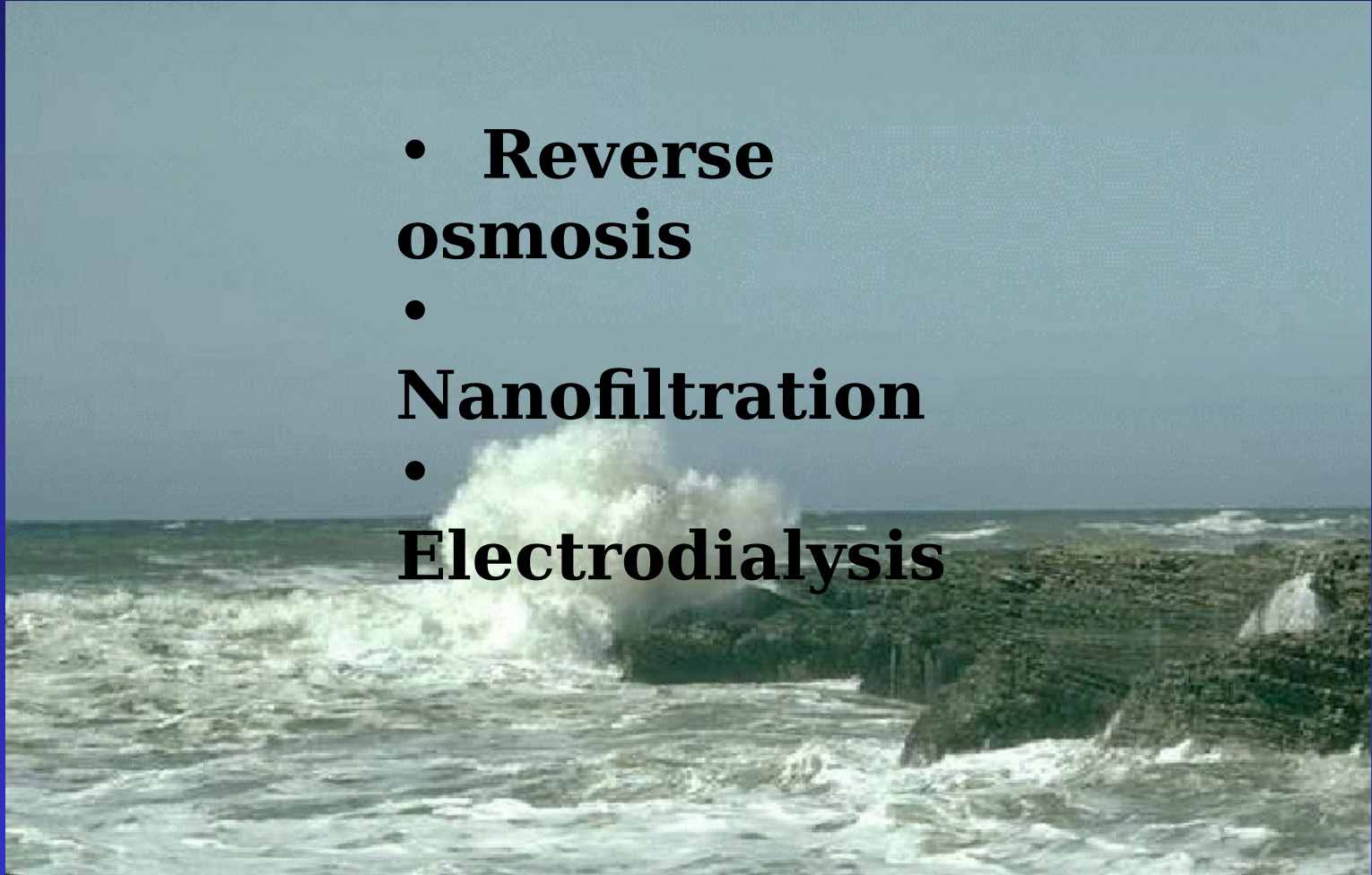
- **Disadvantages**

- Waste disposal from regeneration
- Moderate selectivity
- Distribution system effects
- Resin lifetime



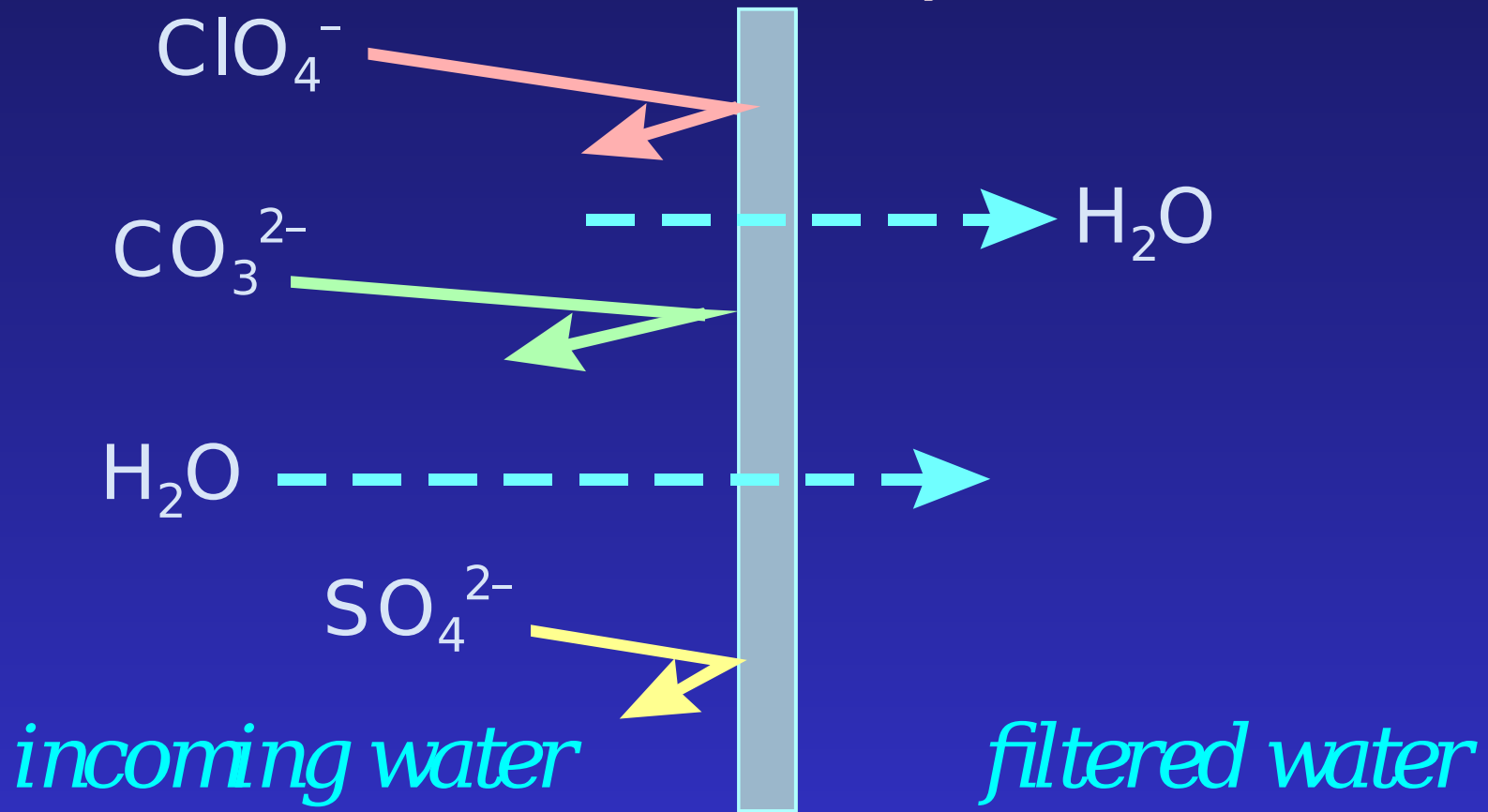
Membrane Techniques

- **Reverse osmosis**
- **Nanofiltration**
- **Electrodialysis**

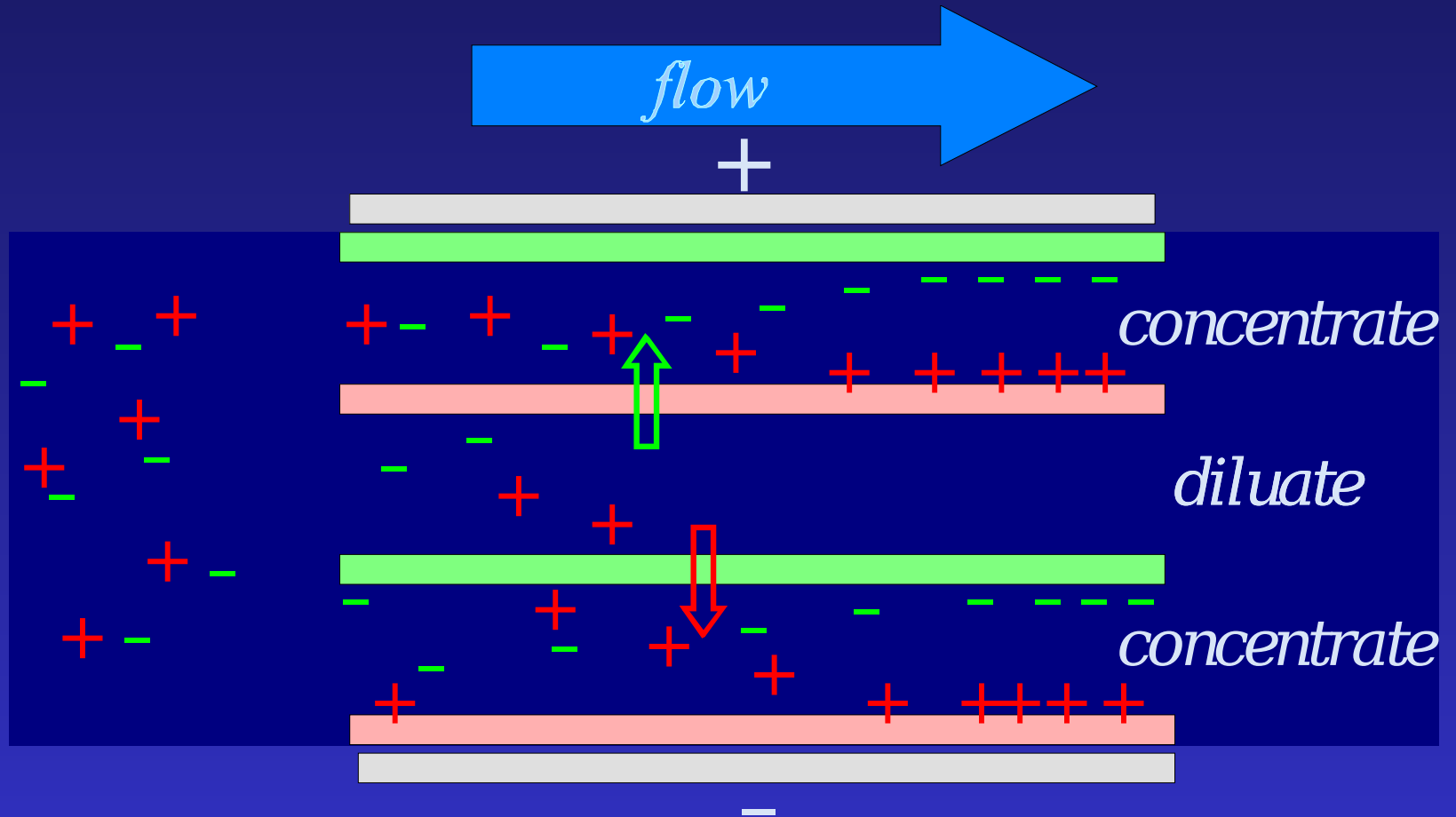


Reverse Osmosis/Nanofiltration

membrane filter



Electrodialysis



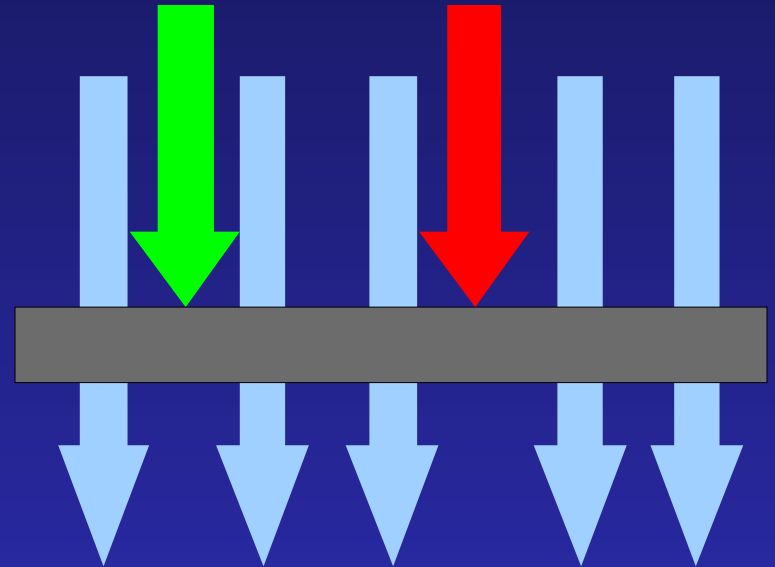
Membrane Techniques

- **Advantages**

- High effectiveness
- Low operating cost
- High throughput
- Easy implementation

- **Disadvantages**

- Low selectivity
- Distribution system effects
- Palatability
- Waste effluent disposal



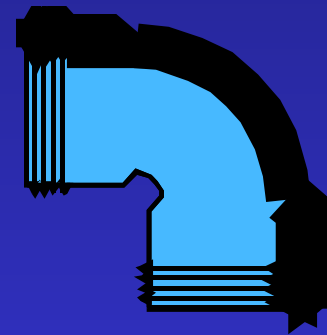
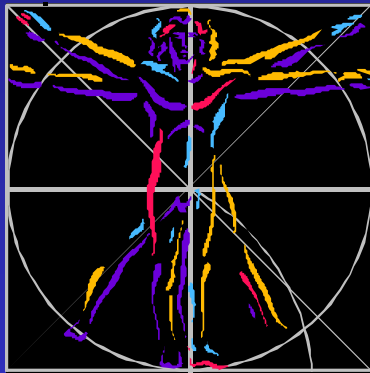
Under Investigation

- Reverse Osmosis and Nanofiltration
- Ozone/GAC (Chemical Reduction?)
- Biological Reduction
- Anion Exchange

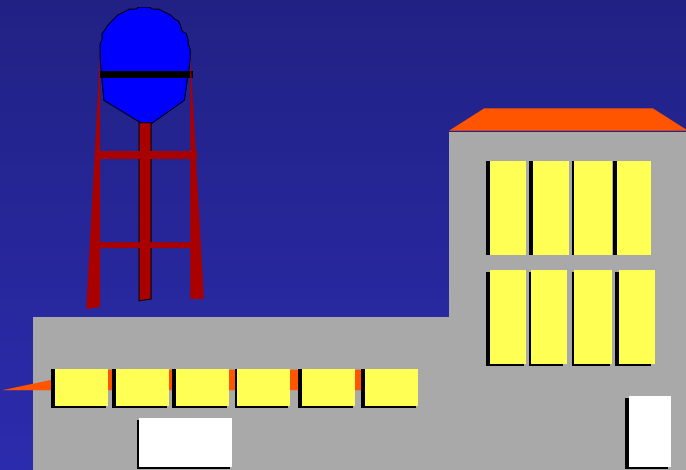


General Considerations

- **Incomplete health effects studies**
- **Success at reaching trace concentrations**
- **Distribution system effects**



General Considerations



- **Effects on other treatment processes**
- **Effects from other treatment processes**
- **Reliability**

General Considerations



- Palatability
- Time
- Expense



Customization



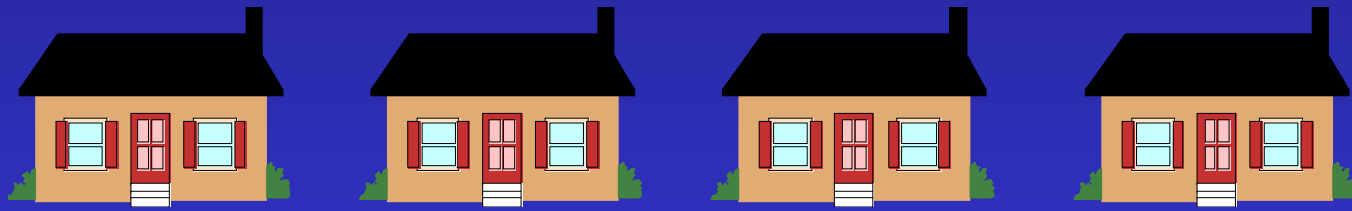
The best solution for a specific situation is likely to be a combination of technologies.

- Anion exchange + bioremediation
- Nanofiltration + blending

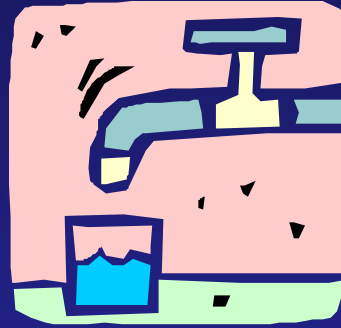
Small Systems

Small systems may benefit from a number of techniques that will not work in large systems.

- Reverse osmosis
- Anion exchange

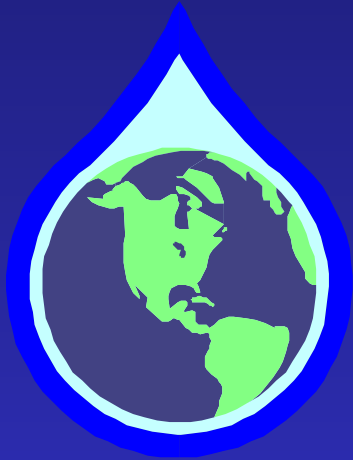


Point of Use



- Some techniques lend themselves to point-of-use devices.
- Both anion exchange and RO may be used at individual sites or for very small systems.
- No standards presently exist for purification systems; however, that could be rectified fairly

Directions



Congress has appropriated \$2 million to the East Valley Water District for studies on perchlorate.

The American Water Works Association Research Foundation has requested proposals.

EPA anticipates an initiative in fiscal year 2000.

Closing

- **Perchlorate is unlike other contaminants already regulated.**
- **Effective management will require long and short term responses.**
- **The best solutions will only come about through continued cooperation among state, local, and federal agencies.**

